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Article

Source apportionment of PAHs in Central European soils with compound-specific triple isotopes (^{13}C , ^{14}C & ^2H)

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4 **Source apportionment of PAHs in Central European soils with compound-**
5 **specific triple isotopes ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ & $\delta^2\text{H}$)**

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23 **ABSTRACT**

24 This paper reports the first study applying a triple-isotope approach for source apportionment
25 of polycyclic aromatic hydrocarbons (PAHs). The $^{13}\text{C}/^{12}\text{C}$, $^{14}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ isotope ratios of
26 PAHs were determined in forest soils from mountainous areas of the Czech Republic,
27 European Union. Statistical modeling applying a Bayesian Markov Chain Monte Carlo
28 (MCMC) framework to the environmental triple isotope PAH data and an end-member PAH
29 isotope database allowed comprehensive accounting of uncertainties and quantitative
30 constraints on the PAH sources between biomass combustion, liquid fossil fuel combustion,
31 and coal combustion at low and high temperatures. The results suggest that PAHs in this
32 central European region had a clear predominance of coal combustion sources ($75 \pm 6\%$;
33 uncertainties represent 1 SD), mainly coal pyrolysis at low temperature ($\sim 650\text{ }^\circ\text{C}$) ($61 \pm 8\%$).
34 Combustion of liquid fossil fuels and biomass represented $16 \pm 3\%$ and $9 \pm 3\%$ of the total
35 PAH burden (ΣPAH_{14}), respectively. Although some soils were located close to potential
36 PAH point sources, the source distribution was within a narrow range throughout the region.
37 These observation-based top-down constraints on sources of environmental PAHs provides a
38 reference for both improved bottom-up emission inventories and guidance for efforts to
39 mitigate PAH emissions.

40 Keywords: Bayesian statistics, polycyclic aromatic hydrocarbons, coal combustion,
41 radiocarbon, stable carbon isotope, stable hydrogen isotope

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46 INTRODUCTION

47 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous, predominantly anthropogenic,
48 organic molecules of environmental concern due to the mutagenic and carcinogenic properties
49 of some congeners (e. g., benzo[a]pyrene)¹. Therefore, owing to their toxicity, they can pose a
50 threat to humans and the environment. Although PAHs are present in uncombusted petroleum
51 (i.e., petrogenic PAHs), the most important sources of PAHs in the environment are from the
52 incomplete combustion of biomass (e.g., wood) and fossil fuels (e.g., petroleum and coal)
53 (i.e., pyrogenic PAHs)^{2,3}. In addition to their own negative effects, PAHs have also been
54 extensively used as molecular tracers of combustion-related airborne particles^{3,4}, which cause
55 numerous human health problems (e.g., lung cancer, respiratory and heart diseases)^{5,6}. Among
56 atmospheric contaminants, PAHs account for most (35-82%) of the total mutagenic activity of
57 airborne particles⁷ and hence, a reduction of PAH emissions is essential to improve air
58 quality.

59 Potential sources of airborne PAHs are vehicle exhaust, power generation, residential
60 heating/cooking, abrasion of tires and asphalt surfaces, waste incineration, and industrial
61 processes. A better understanding of PAH sources is essential to mitigate air pollution, but
62 unfortunately the relative contributions of different sources to PAHs are still poorly
63 understood. A variety of techniques to apportion sources of PAHs exist in the literature, based
64 on either molecular or isotopic compositions³. For instance, numerous studies have used
65 diagnostic ratios of PAH concentrations, usually isomeric ratios, to infer PAH sources^{3,8,9}.
66 However, the molecular composition of PAHs is affected by differential atmospheric removal
67 and transformation processes⁹⁻¹¹. Furthermore, these isomeric ratios are not source specific
68 and show considerable intrasource variability⁹. The intrinsic carbon isotope composition of an
69 individual PAH molecule is a more conservative source tracer¹²⁻¹⁵. Although $\delta^{13}\text{C}$ analysis on
70 individual PAHs is a well-established technique^{12,16,17}, combining both compound-specific

stable isotope and (natural abundance) radiocarbon analyses (CSIA and CSRA, respectively) offers a potentially far more powerful tool for quantitatively determining the sources of contaminants in the environment. In the literature, combined compound-specific $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ measurements have been applied to apportion PAH sources in sediments^{13,14}, soils¹⁸ and air^{15,19-22}. Introducing more isotope systems would naturally offer further improvements in PAH source constraining capacity. As with any mass-balance approach the number of sources that can be differentiated by N markers is N+1. Thus, the advantage of triple-isotope analysis is that we can resolve four sources, rather than two (one marker) or three (two markers). Sun and collaborators²³ reported the potential use of the stable hydrogen isotope in combination with carbon isotopes for source apportionment of PAHs, but very few $\delta^2\text{H}$ -PAH measurements in both emissions and ambient samples have been published to date. The only $\delta^2\text{H}$ determinations performed in ambient emissions was limited to naphthalene, the simplest PAH, from emissions of a combustion process in an alumina refinery²⁴. Combining both stable carbon and radiocarbon isotopes, with the hydrogen isotope analyses represents a promising approach for elucidating sources of PAHs.

The aim of the present study is to demonstrate the triple-isotope approach ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$, $\delta^2\text{H}$) for the source apportionment of different PAHs by application to forest soils from the Czech Republic. The Czech Republic is considered one of the most industrially-developed countries among the new member states of the European Union and is used here as a representative for Central Europe. The reason for studying the soil compartment is that PAHs in soil reflect a longer-term input of pollutants compared to airborne concentrations. To the best of our knowledge, by analyzing simultaneously three isotopes (stable carbon and hydrogen, and radiocarbon), this study represents the first compound-specific application for source apportionment using a triple-isotope approach.

EXPERIMENTAL SECTION

Study Area. Ten forest soil samples from mountainous sites within Czech Republic were collected during September 2009 (Figure 1, Table 1). These mountain soils, which have been repeatedly studied since 1995²⁵, mainly reflect atmospheric transport and deposition. Three samples (#1, #2 and #3) were collected in the north-western part of the country. This border region shared by Germany, Poland and Czech Republic and known as the “black triangle”, is characterized by extremely high levels of pollutant emissions²⁶. Sample #1 was taken from the Krušné Mts., relatively close to the town Litvínov, site of the largest oil refinery in the Czech Republic. Three more samples (#4, #5 and #6) were collected in the Moravian Region (NE Czech Republic). Two of them (#5 and #6) in the Beskydy Mts., located at the border with Slovakia and adjacent to the industrial centers of Valasske Mezirici and Ostrava, which contain a coal tar refinery (DEZA Corporation), a black carbon production plant (CABOT CS) and seven hard coal mines (OKD Corp.). Sample #7 was collected near the observatory of Košetice, a regional background station for international and national air monitoring programmes. Samples #8, #9 and #10 were forest soils from the Bohemian Region (SW Czech Republic), the Czech Bavarian forest. Spruce trees were the main vegetation type found in all sampling sites. Details on soil sampling are described in the supplementary material.

Quantification of PAHs. Analyses of PAHs were performed at the Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic. Briefly, an aliquot of ca. 10 g dry soil was extracted using automated warm Soxhlet extraction with dichloromethane (DCM). The extract was cleaned-up using activated silica flash column chromatography and analytes eluted with DCM. The eluate was concentrated using a stream of nitrogen in a concentrator unit, and transferred into a mini vial. Before injection, an internal standard of terphenyl was added. Samples were analyzed by a 6890N GC (Agilent, USA) capillary gas chromatography coupled to a mass spectrometer 5973N MS (Agilent, USA)

using electronic ionization (70 eV). PAHs were analyzed by selective ion recording (SIR). Further details on sample extraction, clean-up, instrumental analysis and quality control procedures are included in the supplementary material.

Extraction of PAHs for Isotope Analysis. Sample extraction for the isotope analysis was performed at RECETOX, Brno, Czech Republic. Based on the concentrations found in the individual soil samples in the previous step, the soil sample size needed to provide a sufficient quantity of selected PAHs was determined. It varied between 500 and 1500 g of soil among the top soil samples. Soxhlet-extracted samples with DCM were pre-cleaned using large volume silica gel columns and concentrated. As the mountain forest soils contain large amounts of organic material, additional clean-up was needed. Gel-permeation chromatography was applied to remove high molecular weight compounds from the samples. Samples were concentrated to a final volume of 1 ml for further isotope analyses. Further information on these clean-up procedures is provided in the supplementary material. It has been showed and reported that these purification procedures do not affect the original molecular isotopic signatures. Results from studies on isotope fractionation during purification procedures are included in the supplementary material.

Isolation of PAHs for Radiocarbon Analysis. Isolation of PAHs from soil extracts was carried out at Stockholm University as previously described^{14,27,28}. Extracts were repeatedly injected onto a preparative capillary gas chromatography (pcGC) system programmed to trap selected PAHs^{14,29,30}. The pcGC system consisted of a gas chromatograph coupled to a flame ionization detector 6890N GC (Agilent, Palo Alto, USA) and an autoinjector (7683A, Agilent) integrated with a Gerstel cooled injection system (CIS), a zero-dead volume effluent splitter and a Gerstel preparative trapping device. Since the abundance of the target PAH compounds present in these soil samples was quite low relative to the requirements for ¹⁴C measurements (~20-100 µg), individual PAHs were pooled and trapped as follows: 1.

Phenanthrene (PHEN) + anthracene (ANTH); 2: fluoranthene (FLU) + pyrene (PYR); 3: benz[a]anthracene (BaA) + triphenylene (TP) + chrysene (CHRY); 4: benzo[b]fluoranthene (BbF) + benzo[j]fluoranthene (BjF) + benzo[k]fluoranthene (BkF); 5: benzo[e]pyrene (BeP) + benzo[a]pyrene (BaP); 6: indeno[1,2,3-cd]pyrene (IcdP) + benzo[ghi]perylene (BghiP). Additional details about chromatographic conditions and trapping procedures are included in the Supporting Information.

Analysis of Stable Carbon and Hydrogen Isotopes. $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses of soil extracts were performed at The University of Bristol, UK. The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope ratio determinations were performed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS). $\delta^{13}\text{C}$ analyses were performed using a ThermoQuest Finnigan DeltaPlusXL IRMS coupled to an Agilent 6890 GC *via* a ThermoQuest Finnigan GC Combustion III interface. $\delta^2\text{H}$ determinations were performed using a Thermo DeltaVPlus IRMS coupled to a Trace GC *via* a GC Isolink and ConFloIV interface. For both $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses, chromatographic peaks were integrated in groups using the same ‘chromatographic windows’ described above corresponding to those compounds which were isolated by pcGC, so as to accurately represent the content of the samples analyzed by accelerator mass spectrometry (AMS). The reported isotopic results, expressed in the per mil deviation (‰) of the isotope ratio from the standards Peedee belemnite (PDB) and Vienna Standard Mean Ocean Water (VSMOW) for C and H, respectively, represent the arithmetic means of triplicate analyses. Further information on the instrumental analysis and quality procedures is provided in the supplementary material.

Analysis of Radiocarbon. The extracts for ^{14}C analysis were shipped to the US National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility (Woods Hole, MA, USA). The pcGC isolates were first purified, then combusted at 850 °C for its conversion to carbon dioxide and finally reduced to graphite. Targets of graphite were analyzed for ^{14}C by AMS according to standard procedures³⁰⁻³². All ^{14}C determinations are expressed as the per

171 mil (‰) deviation from NBS oxalic acid I. Further details about the ^{14}C analysis are included
172 in the Supplementary Information.

173 **Bayesian Markov Chain Monte Carlo method for source apportionment.** The three-
174 dimensional isotope signatures of the different PAHs were used in an isotopic mass balance
175 source apportionment model to differentiate four main sources: biomass, liquid fossil (e.g.,
176 petroleum and oil), low temperature ($\sim 650\text{ }^{\circ}\text{C}$) coal combustion and high temperature (~ 900
177 $^{\circ}\text{C}$) coal combustion, largely following our earlier dual-isotope (three source)
178 approaches^{15,33,34}. The current study's four sources were selected based on two criteria: 1)
179 they encompass the majority of PAHs emitted in this region³⁵, 2) they are differentiable by
180 means of $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ and $\delta^2\text{H}$ isotopic signatures. In particular, we note that PAHs emitted
181 from high temperature coal combustion are more depleted in ^{13}C while more enriched in ^2H ,
182 compared to coal combustion at lower temperatures¹⁷.

183 The source-specific isotope values (end members) were collected from the literature, and are
184 summarized in Table S1. These end members are associated with significant variability and
185 uncertainties, especially in the $\delta^2\text{H}$ dimension. Such variability has recently been shown to
186 affect not only the precision of the source apportionment calculations, but also the estimated
187 central values (e.g., mean and median) of the source fractions³³. To account for this variability
188 a Bayesian Markov Chain Monte Carlo (MCMC) approach was implemented³⁶, in which the
189 end member distributions are modelled as normal distributions with mean and standard
190 deviation defined by the literature values. The source-specific isotope values used in the
191 present study are listed in Table 2 and its calculation is detailed in the Supporting
192 Information. The MCMC approach effectively samples the 4-dimensional fractional source
193 space while satisfying the mass-balance criterion and accounting for the end member
194 variability. The result of the Bayesian approach is a probability density function (pdf) of the
195 relative source contribution for each source (Figure 3A). From this pdf the statistical

parameters of interest (e.g., mean, median, standard deviation or confidence intervals) may be computed. The MCMC computations were run using an in-house written MATLAB version 2014a (The MathWorks, Natick, MA, USA) script, with 200,000 iterations, a burn-in (initial search phase) of 10,000 and a data thinning of 10. The details of the Bayesian calculation is published elsewhere³⁴ and the MATLAB script is presented in the present paper's Supporting Information.

RESULTS AND DISCUSSION

PAH Concentrations and Composition. The PAHs input to mountain soils is mainly through dry or wet deposition of aerosol particles or residues of vegetative litter, and by processes of air-soil partitioning^{37,38}. Forest soils are usually rich in organic matter, which favors the accumulation of PAHs. The content of PAHs (sum of 14 PAHs) in the central European forest soils ranged from 0.53 to 9.1 $\mu\text{g}\cdot\text{g}^{-1}$ ($4.3 \pm 2.8 \mu\text{g}\cdot\text{g}^{-1}$, $\mu \pm \sigma$)(Table 1). These concentrations were in agreement with previously reported concentrations at the same sampling sites^{25,39} (1.7-8.2 $\mu\text{g}\cdot\text{g}^{-1}$). As was expected from their proximity to emission sources, the highest PAH loadings were observed at both northwestern (7.4 and 5.5 $\mu\text{g}\cdot\text{g}^{-1}$ for #1 and #2 respectively) and eastern border regions (9.1 and 5.9 $\mu\text{g}\cdot\text{g}^{-1}$ for #5 and #6, respectively). The lowest concentrations were found at Mt. Sumava, close to the border region shared with Germany-Czech Republic-Austria (#9, 0.53 $\mu\text{g}\cdot\text{g}^{-1}$) and at the regional site of Kosetice (#7, 0.87 $\mu\text{g}\cdot\text{g}^{-1}$). All samples, except for #9, had a PAH content slightly higher than reported for other remote/forest sites in Europe, such as in the Pyrenees⁴⁰ (0.77 $\mu\text{g}\cdot\text{g}^{-1}$), Alps⁴¹ ($1.3 \pm 0.6 \mu\text{g}\cdot\text{g}^{-1}$) and Tatras⁴¹ ($1.6 \pm 0.4 \mu\text{g}\cdot\text{g}^{-1}$). However, these border mountain soils may be also affected by long range transport contamination coming from Poland, Germany, Slovakia or Austria besides Czech Republic⁴².

Relative PAH concentrations (Diagnostic Ratios, DR) are typically used for conventional semiquantitative source apportionment through the comparison of the ambient ratios with specific PAH source signatures. However, PAHs are affected by different atmospheric processes and therefore the relative proportions of the PAH species are not conserved between the emission source and the receptor site¹⁰. It is known that ANTH, BaA and BaP are photochemically less stable in the atmosphere than PHEN, CHRY and BeP^{43,44}. In the present study, DRs were used to assess the extent of photochemical degradation of the studied samples. Microbial degradation of PAHs that may change their isomer composition in background surface soils is deemed unlikely to have a substantial effect on the source apportionment results, considering the limited degradation observed in soils with high content of organic matter affected by diffuse PAH pollution⁴⁵. The BaA/(BaA+CHRY) and BaP/(BeP+BaP) ratios ranged from 0.09 to 0.26 and from 0.13 to 0.44, respectively, and correlate positively ($R^2 = 0.90$) (Table S2). Samples #1, #6 and #7 showed the largest observed DRs (BaA/(BaP+BeP)>0.40 and BaA/(BaA+CHRY)>0.26, Table S2), indicating that PAHs had been transported the shortest distance from the source. In contrast sample #10 presented the lowest ratios, thus the largest distance to the source.

Carbon Isotope Composition of PAHs in Soils. Compound-specific stable carbon isotope is used to apportion sources. Polycyclic aromatic hydrocarbon (PAH) extracts from all samples were analyzed for their stable carbon isotope composition ($\delta^{13}\text{C}$). The $\delta^{13}\text{C}$ values ranged between -25.3‰ and -23.0‰ ($-24.0 \pm 0.1\text{‰}$, $\mu \pm \sigma$) (Table 1 and Table S3). No substantial variation was observed among sampling sites, which suggests a relatively homogenous source. However, there was a consistent $\delta^{13}\text{C}$ variability between the different PAH compounds, with the PAH group BaA + TP + CHRY (m/z 228) having the highest $\delta^{13}\text{C}$ values ($-23.4 \pm 0.3\text{‰}$) and the PAH group IcdP+BghiP (m/z 276) having the lowest $\delta^{13}\text{C}$

values ($-24.6 \pm 0.3\text{‰}$) (Figure 2A). This suggests that generation processes differed for the different PAH molecules. During polyaromatization reactions, ^{13}C is preferentially lost during C=C bond formation leading to a relative depletion in $\delta^{13}\text{C}$ values⁴⁶. However, no positive correlation was observed between molecular weight and $\delta^{13}\text{C}$ values. Overall the $\delta^{13}\text{C}$ values of the PAHs in the present study were comparable to those observed in aerosols from Chinese cities⁴⁷ (-26.3 to -24.4‰ in Chongqing and Hangzhou and -25.5 to -23.5‰ in Beijing) and soils from a domestic coal-burning village near Glasgow, UK⁴⁸ (-25‰). $\delta^{13}\text{C}$ were, however, generally more enriched in ^{13}C relative to ambient samples from other European countries such as Sweden¹⁵ (-28.9‰), Croatia²⁰ (-29.2‰) or Greece²⁰ (-29.0‰) and from archipelago sediments in Stockholm, Sweden¹⁴ (-27.0 to -24.8‰).

The radiocarbon content was determined for only those samples with sufficient analyte concentrations ($n = 7$ sites). The determined $\Delta^{14}\text{C}$ values ranged between -960‰ and -768‰ ($-892 \pm 37\text{‰}$) (Table 1 and Table S4). The radiocarbon composition exhibited very low variability between different sampling sites and PAH compounds (Figure 2B), suggesting a relatively homogenous source, which is consistent with the ^{13}C data. These highly depleted ^{14}C signatures confirm that PAHs in these Czech forest soils are of a mainly fossil fuel origin. Although the soil sample from Kosetice (#7) had slightly more modern carbon (less negative signal) (-819‰ , Table 1), those samples with the highest concentrations of PAHs had $\Delta^{14}\text{C}$ values reflecting the largest fossil fuel contribution (#1, #2, #5 and #6 with $\Delta^{14}\text{C} \sim -942$ and -897‰ , Table 1). Whereas the Czech border sites are mostly affected by long-range transport of pollutants from industrial regions, more local impact is expected in Kosetice (#7). This regional site belongs to an agricultural region with several small villages within 5-10 km in all directions where wood is usually burned for domestic heating. PAHs in Czech Republic had generally very high fossil contributions compared to PAHs from many other worldwide sites, e.g., rural and background sites in Sweden^{15,20} (-138 to $+58\text{‰}$ and -388 to -381‰ ,

respectively), western Balkans²² (-568 to -288‰) and even a residential area in Tokyo¹⁹ (-514 to -787‰). However, the $\Delta^{14}\text{C}$ -PAH values were similar to airborne PAHs from Croatia²⁰ (-888‰), Greece²⁰ (-914‰), Alabama, US²¹ (-980‰) and sediments from Stockholm, Sweden¹⁴ (-891 to -709‰).

Hydrogen Isotope Composition of PAHs in Soils. This is the first study complementing the earlier reported dual compound-specific carbon isotope system of PAHs^{14,15,22} with hydrogen stable isotopic analyses. The PAH extracts exhibited $\delta^2\text{H}$ values between -263‰ and -53‰ (-129 \pm 44‰) (Table 1 and Table S5). In contrast to both carbon isotope systems ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$), the deuterium system showed a higher variability among sampling sites. The western border soil (#1) had a relatively much more ^2H -depleted value (-226‰) compared to #5 ($\delta^2\text{H} \sim 135$ ‰) or the remaining studied soils (#2, #6, #7, #8 and #10, $\delta^2\text{H} \sim -109$ ‰). Other studies have suggested that deuterium enrichment takes place simultaneously with ^{13}C depletion during PAH generation²³. However, in the present study no correlation was found between PAH $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values. Furthermore, no significant variability was observed between the $\delta^2\text{H}$ values and the different PAHs (Figure 2A). Therefore, these data suggest that the relatively more ^2H -depleted signature at site #1 reveals a PAH source different from the other soils. To date, there have been no other studies on $\delta^2\text{H}$ values of PAHs in modern soils.

Monte Carlo Simulations for Source Apportionment. The compound-specific triple-isotope approach allowed elucidation of up to four different sources. In the present study three isotope signatures were analyzed, $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ and $\delta^2\text{H}$, for PAHs in forest soils from the Czech Republic. The stable carbon isotope ($\delta^{13}\text{C}$) is a priori informative for source apportionment but it also has been shown that atmospheric photochemical processes can lead to ^{13}C shifts^{49,50}. However, O'Malley and collaborators evaluated the effects of evaporation, photodecomposition and microbial degradation on the $\delta^{13}\text{C}$ values of individual PAHs and no significant alterations were observed¹². Furthermore, in the present study, no correlation was

found between the diagnostic ratios for photochemical degradation (BaA to BaA + CHRY and BaP to BaP + BeP) and their respective $\delta^{13}\text{C}$ values (Figure S1). Based on this analysis, carbon isotopic fractionation of PAHs during atmospheric transport was therefore likely insignificant and $\delta^{13}\text{C}$ values were used to apportion PAH sources.

The natural abundance of radiocarbon ($\Delta^{14}\text{C}$) was utilized to differentiate between fossil fuel (-1000‰) *versus* combustion of contemporary sources ($+137.5 \pm 21.9\%$) for PAHs. Stable carbon isotope ratio determinations of individual PAHs showed different $\delta^{13}\text{C}$ values for the combustion of C_3 terrestrial vegetation⁵¹⁻⁵³ (e.g., wood, $\sim -28.7\%$) and liquid fossil fuels^{23,52,54} (e.g., gasoline, $\sim -24.1\%$, diesel, $\sim -26.5\%$). Regarding the individual PAHs derived from coal combustion sources, $\delta^{13}\text{C}$ values have been shown to vary over a wide range by ca. 8‰^{17,23,52,55-57} (-31 to -23‰) and overlapping with C_3 wood and liquid fossil fuel sources. The $\delta^{13}\text{C}$ values of coal-derived PAHs are normally dictated by both the isotopic signature of the parent fuels and the temperature of combustion. In general, PAHs derived from carbonization processes at low temperatures ($\sim 650\text{ }^\circ\text{C}$) have isotopic values similar to those of the parent coals^{17,52,58-60} (-25.4 to -21‰), because they are mainly primary devolatilisation products from mild combustion processes¹⁷. Instead, $\delta^{13}\text{C}$ values of PAHs became lighter when the temperature of carbonization is higher ($\sim 900\text{ }^\circ\text{C}$) because they are then products of condensation reactions, which result in a kinetic isotope effect with ^{12}C - ^{12}C bonds forming more easily than ^{13}C - ^{12}C bonds^{17,23,52,55} (-29.4 to -24.2‰).

In contrast to their $\delta^{13}\text{C}$ values, the $\delta^2\text{H}$ values of PAHs generated by coal, biomass and liquid fuel pyrolysis differ substantially (e.g., liquid fossil fuels^{23,53}, -76 to -47‰; C_3 wood⁵³ $\sim -94\%$; high coal pyrolysis²³, -81 to -65‰; bulk coals^{58,60}, -170 to -87‰; and bulk peat⁶¹⁻⁶³, -240 to -79‰). However, only few source-specific $\delta^2\text{H}$ values have been reported in the scientific literature to date. Therefore, in the future there is the need to better characterize the hydrogen isotopic signature of primary sources. Although $\delta^2\text{H}$ literature values are currently

limited, the simultaneous use of $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ and $\delta^2\text{H}$ provide a greater differentiation and allowed quantitatively to apportion the relative contribution of four different combustion source classes to the PAH. Source-specific $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values reported in literature are summarized in the Supporting Information (Table S1).

The choice of sources to perform the Bayesian-based method (see Experimental Section) was based on existing bottom-up emission inventories and past PAH fingerprinting studies indicating the major sources of PAHs in the Czech Republic^{35,64-66}. By combining the isotopic signatures of sample data and primary PAH sources in two-dimensional plots (Figures 2A+B), the following four sources were chosen: combustion of liquid fuels, C_3 wood combustion, as well as coal combustion at low ($\sim 650\text{ }^\circ\text{C}$) and high ($\sim 900\text{ }^\circ\text{C}$) temperatures. The isotopic signatures used for the primary PAHs sources are detailed in Table 2.

Natural peat fires in the border mountainous Czech areas were a priori a potential source of PAHs in Czech Republic. However, the present PAH-isotope data did not support this hypothesis (Figure 2A+B). Furthermore, the soil from the northwestern part of the country (#1) had a hydrogen stable-isotope composition which was more depleted in ^2H than the other samples and moreover, did not match any of the primary sources explored for $\delta^2\text{H}$ values of PAHs in the literature to date (Figure 2A+B). Shifts in the $\delta^2\text{H}$ values of organic molecules have been observed as a result of many degradation processes with potentially quite large enrichment factors⁶⁷. However, such deuterium fractionation is generally accompanied with a shift also in the $\delta^{13}\text{C}$ values, which was not observed in the case of sample #1. It is worth noting here that the lack of reported source-specific data for the hydrogen isotope composition makes it difficult to draw other interpretations of sample #1. As a result, sample #1 was not considered for the Bayesian-based data analysis due to the inability to associate its $\delta^2\text{H}$ values to either a primary source or a degradation process. Nevertheless, the results of the radiocarbon analyses of site #1 enabled the calculation of the relative contributions of the

344 combined fossil fuel sources *versus* contemporary biomass using a simple isotopic mass
345 balance equation as described elsewhere¹⁴ (Table 3 and Figure 3B).

346 The compound-specific isotope ratios for every site were combined with literature values for
347 source end members in a mass balance-based source-apportionment scheme. The variability
348 of the isotopic source signatures were accounted for within a Bayesian Markov Chain Monte
349 Carlo framework. Four probability density functions, one for every source, were obtained for
350 every group of PAHs and site (#2, #5, #6, #7, #8 and #10), as is shown at Figure 3A for the
351 group BbF+BjF+BkF and site#7. All samples showed a similar source pattern with the highest
352 contribution coming from the coal combustion at low temperature, ranging from 53 to 75%
353 ($61 \pm 8\%$, Table 3 and Figure 3B). Practically equal contributions from liquid fossil fuels and
354 coal combustion at high temperature were also observed for all samples ($16 \pm 3\%$ and $13 \pm$
355 2% , respectively). Biomass combustion was the least important source of PAHs in Czech
356 Republic soils, with contributions ranging between 5 to 16% ($9 \pm 3\%$). Only small differences
357 were observed between samples, but those soils with the highest PAH concentrations from the
358 northwestern (#1 and #2) and the eastern border (#5 and #6) regions had slightly higher coal-
359 related contributions (Figure 3B, high + low temperatures coal combustion $\sim 74\text{--}85\%$ and
360 biomass $\sim < 9\%$). Correspondingly, soils from Kosetice and the southern region had slightly
361 higher biomass contributions (#7, #8 and #10, biomass $\sim 10\text{--}16\%$ and coal $\sim 66\text{--}74\%$).
362 Although some soil sites were placed relatively close to potential PAH point sources and
363 showed higher PAH concentrations, the triple-isotope-based apportionment demonstrated that
364 the contribution from the four different source classes were rather homogeneous for
365 mountainous forest soils across the country. The low observed biomass contributions ($9 \pm$
366 3%) in Czech background soils are similar to those observed in South Europe, such as in
367 background air from Croatia and Greece²⁰ (9% and 7% , respectively), but lower than those in
368 North Europe (i.e. Sweden²⁰, 50%)

Coal combustion at low and high temperatures may be associated to domestic and industrial emissions, respectively. Additionally, combustion of fuels at low temperature has the potential to result in higher PAH emissions than high-temperature combustion sources (i.e. the lower is the combustion temperature, higher are the PAHs emission factors⁴). These high emission factors might explain the high contribution coming from low-temperature coal combustion sources in Czech Republic. However, the household coal usage represents only the 3% of the total coal production in the Czech Republic⁶⁸. Furthermore, the residential coal burning represents one of the most toxic sources of PAHs due to both high emission rates and proximity to population³⁵. Emission inventories show a reduction of PAH emissions in recent years in almost all European countries, being the residential sector the most important source of PAHs nowadays³⁵. In 2007, residential emissions (including fossil and non-fossil sources) accounted for the 47.5% of the total PAH emissions in Europe³⁵. The present study shows like the residential sector in Czech Republic, in particular the residential coal burning, may be more important than the European average. Taken together, PAHs in Czech soils are heavily influenced by coal combustion practices (75%), mainly coming from household emissions (61%).

The present study demonstrates firstly that triple isotope characterization of PAHs is possible and secondly, that this information is useful for source characterization. However, the existing literature on isotope characterization of PAHs is currently limited. We think and hope that the current contribution may encourage researchers to expand the existing source database. Such work should seek to both improve the statistics for the currently investigated sources, but also expand the number of source categories in terms of their geographical prevalence.

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SUPPORTING INFORMATION AVAILABLE

Table S1. Compilation of literature values for isotopic signatures of primary sources

Table S2. Individual PAH concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) in forest soils from Czech Republic

Table S3. $\delta^{13}\text{C}$ values of PAHs in forest soils from Czech Republic

Table S4. $\Delta^{14}\text{C}$ values of PAHs in forest soils from Czech Republic

Table S5. $\delta^2\text{H}$ values of PAHs in forest soils from Czech Republic

Figure S1. Relation between the ratio BaA to BaA + CHRY and the $\delta^{13}\text{C}$ values of the “chromatographic window”: BaA + CHRY (Panel A) and the ratio BaP to BaP + BeP and the $\delta^{13}\text{C}$ values of the “chromatographic window”: BaP + BeP (Panel B)

Figure S2. GC/MS chromatograms depicting the different PAH traps from Sample #1 isolated by pcGC

614 Supplemental Text S1. Experimental section

615 Supplemental Text S2. Calculation of the isotopic signatures (end members) for the primary

616 PAHs sources

617 Supplemental Text S3. MATLAB script for the Bayesian calculation

618 This information is available free of charge via the Internet at <http://pubs.acs.org>.

Table 1. PAH concentrations and average carbon ($\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) and hydrogen ($\delta^2\text{H}$) values of PAHs in forest soils

Sample ID	Site	Longitude	Latitude	Altitude (m a.s.l. ^a)	$\Sigma\text{PAH}^{\text{b}}$ ($\mu\text{g}\cdot\text{g}^{-1}$ d.w. ^c)	$\delta^2\text{H}$ (‰)	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
#1	Krušné hory-Červená jáma	13° 27.702'	50° 33.804'	840	7.35	-225.8 ± 4.9	-24.18 ± 0.10	-911 ± 87
#2	Lužické hory-Jedlová	14° 33.035'	50° 51.939'	520	5.52	-116.6 ± 3.4	-24.04 ± 0.17	-897 ± 19
#3	Krkonoše-Pašerácký chodník	15° 45.933'	50° 44.416'	1320	2.61		-24.13 ± 0.14	
#4	Jeseníky-Jelení loučky	17° 15.544'	50° 8.867'	1120	2.49		-23.81 ± 0.20	
#5	Beskydy-Kykulka	18° 26.447'	49° 34.523'	930	9.11	-135.5 ± 23.9	-23.94 ± 0.09	-942 ± 24
#6	Javorníky-Kohútka	18° 12.756'	49° 17.713'	811	5.88	-108.6 ± 3.1	-24.04 ± 0.14	-905 ± 18
#7	Košetice	15° 05.476'	49° 34.231'	495	0.872	-99.3 ± 10.6	-24.13 ± 0.17	-819 ± 14
#8	Novohradské hory-Vysoká	14° 44.141'	48° 42.808'	971	3.81	-112.8 ± 3.1	-24.05 ± 0.26	-884 ± 17
#9	Šumava-Boubín	13° 49.018'	49° 0.026'	1120	0.532		-23.97 ± 0.22	
#10	Český les-Čerchov	12° 46.813'	49° 22.946'	985	4.80	-107.0 ± 3.8	-24.19 ± 0.22	-886 ± 14
Average±stdev					4.30 ± 2.77	-129.4 ± 44	-24.05 ± 0.12	-892 ± 37

^a above sea level^b sum of 14 PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, triphenylene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene^c dry weight

Table 2. Isotopic signatures (end members) for the primary PAHs sources^a

Primary Source/ Isotope (mean±stdev, ‰)	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\Delta^{14}\text{C}$
C3 plant combustion ^b	-28.7 ± 1.4	-94 ± 3	$+137.5 \pm 21.9$
Liquid fossil fuel combustion ^c	-25.3 ± 1.6	-62 ± 7.3	-1000 ± 0
Coal pyrolysis at low temperature ($\sim 650\text{ }^\circ\text{C}$) ^d	-23.2 ± 1.1	-129 ± 20.8	-1000 ± 0
Coal pyrolysis at high temperature ($\sim 900\text{ }^\circ\text{C}$) ^e	-26.8 ± 1.3	-73.2 ± 4.0	-1000 ± 0

^a See Table S1 and Text S2 with a literature compilation of isotopic signatures and calculation of the primary PAH sources end members, respectively

^b $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for biomass were calculated as the average between PAH-specific and bulk signatures found in the literature. Three and one literature sources were used for $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively. $\Delta^{14}\text{C}$ for biomass was calculated assuming equal contributions of fresh biomass (+50‰) and wood (+225‰).

^c $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values were calculated assuming equal contributions from diesel and gasoline sources. Five and two literature sources were used for $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively.

^d $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values reported for bulk coal were used as $\delta^2\text{H}$ -PAH and $\delta^{13}\text{C}$ -PAH signatures for coal combustion at low temperature assuming that the PAHs derived from carbonization processes at low temperatures have isotopic values similar to those of the parent coals. Seven and three literature sources were used for $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively.

^e Four and one literature sources were used for $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively.

Table 3. Source contributions of liquid fossil fuel combustion, coal combustion at low and high temperature and biomass combustion for the ΣPAH_{14} in forest soils based on a four-source Bayesian Markov Chain Monte Carlo statistical mass-balance model (mean \pm stdev)

Sample ID	$f_{\text{liquid fossil fuel}}$ (%)	$f_{\text{low T coal}}$ (%)	$f_{\text{high T coal}}$ (%)	f_{biomass} (%)	f_{coal} ($f_{\text{low T coal}} + f_{\text{high T coal}}$) (%)	f_{fossil} ($f_{\text{low T coal}} + f_{\text{high T coal}} + f_{\text{liquid fossil fuel}}$) (%)
#1				7.9		92.1
#2	15.4 \pm 10.3	62.3 \pm 10.4	13.2 \pm 9.6	9.1 \pm 0.2	75.6 \pm 10.3	90.9 \pm 17.5
#5	9.6 \pm 7.3	75.2 \pm 8.8	10.1 \pm 7.6	5.1 \pm 0.1	85.3 \pm 7.3	94.9 \pm 13.8
#6	17.4 \pm 11.6	59.7 \pm 11.2	14.5 \pm 11.0	8.4 \pm 0.2	74.2 \pm 11.6	91.6 \pm 19.5
#7	17.9 \pm 12.3	53.1 \pm 12.1	13.2 \pm 10.6	15.9 \pm 0.3	66.2 \pm 12.5	84.1 \pm 20.4
#8	15.3 \pm 10.6	61.3 \pm 10.5	13.2 \pm 9.6	10.2 \pm 0.2	74.5 \pm 10.6	89.8 \pm 17.7
#10	17.7 \pm 11.9	56.7 \pm 11.4	15.6 \pm 11.0	10.0 \pm 0.2	72.3 \pm 11.9	90.0 \pm 19.8
Average	15.6 \pm 3.1	61.4 \pm 7.6	13.3 \pm 1.8	9.5 \pm 3.3	74.7 \pm 6.2	90.2 \pm 3.5

FIGURE CAPTIONS

Figure 1. Map depicting bottom-up emission inventory of total 16 PAHs in 2007 (grid $0.1^\circ \times 0.1^\circ$)³⁵. The sampling sites are indicated with white triangles.

Figure 2. Two-dimensional dual-isotope presentation of PAH in forest soils from sites #1 (circles), #5 (diamonds), #6 (triangles) and average of #2, #7, #8 and #10 (squares). Panel (A): $\delta^2\text{H}$ versus $\delta^{13}\text{C}$, where symbol colors are based on PAH molecular weight: m/z 178 (dark blue), m/z 202 (light blue), m/z 228 (green), m/z 252 (yellow and orange), m/z 276 (red); Panel (B): $\delta^2\text{H}$ versus $\Delta^{14}\text{C}$, where symbol colors are based on PAH concentrations. Isotopic signatures of primary sources of PAH are shown: biomass combustion (green), peat (light grey), liquid fossil fuel combustion (black), high temperature coal combustion (“high-T coal”, brown) and low temperature coal combustion (“low-T coal”, dark grey). Isotopic signatures on primary sources are based on reported literature values (Tables 2 and S1). Abbreviations: phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP).

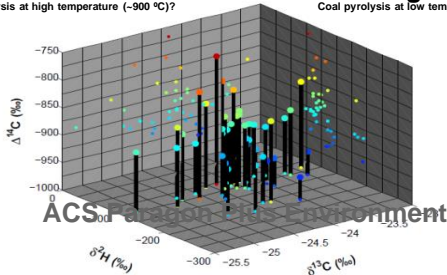
Figure 3. Probability density functions (pdf) of the relative source contribution of PAHs benzo[b+j+k]fluoranthene for Sample #7 (Panel A) and source contributions of fossil (liquid fuel + coal), liquid fossil fuel, coal combustion at low and high temperature and biomass combustion for the sum of PAHs in forest soils from Czech Republic (Panel B).

SOURCE APPORTIONMENT OF PAHs

Environmental Science & Technology

Coal pyrolysis at high temperature (~900 °C)?

Coal pyrolysis at low temperature (~650 °C)?



Liquid fossil fuel combustion?

Biomass combustion?

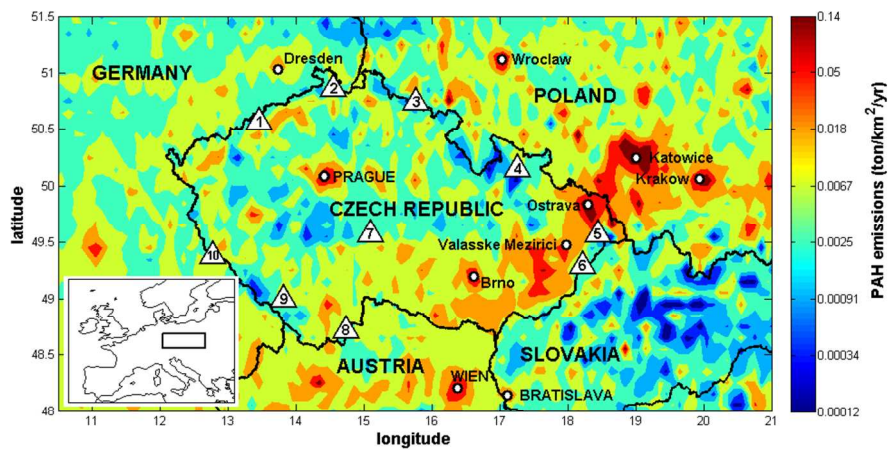


Figure 1. Map depicting bottom-up emission inventory of total 16 PAHs in 2007 (grid $0.1^\circ \times 0.1^\circ$)³⁵. The sampling sites are indicated with white triangles.
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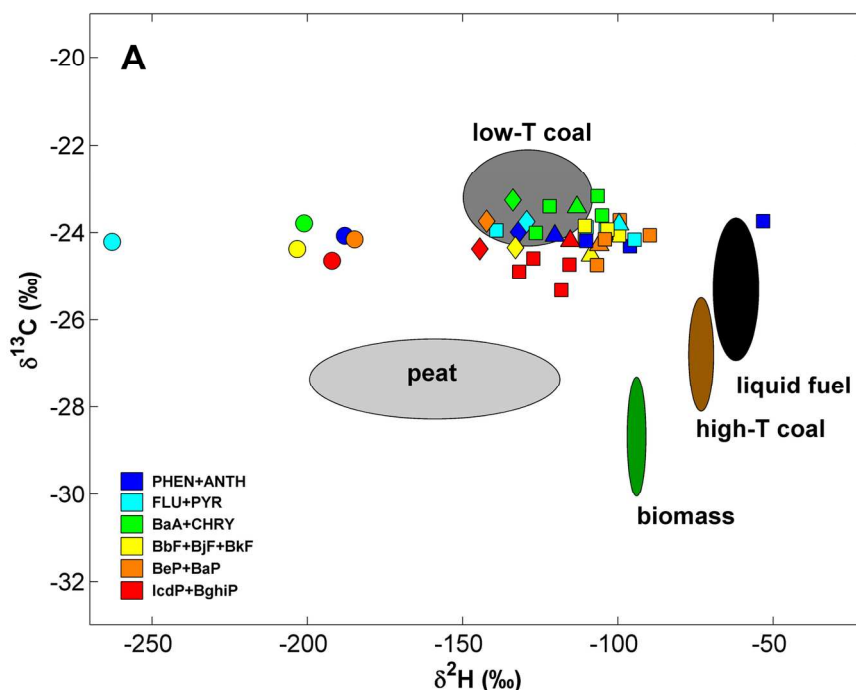


Figure 2. Two-dimensional dual-isotope presentation of PAH in forest soils from sites #1 (circles), #5 (diamonds), #6 (triangles) and average of #2, #7, #8 and #10 (squares). Panel (A): $\delta^2\text{H}$ versus $\delta^{13}\text{C}$, where symbol colors are based on PAH molecular weight: m/z 178 (dark blue), m/z 202 (light blue), m/z 228 (green), m/z 252 (yellow and orange), m/z 276 (red); Panel (B): $\delta^2\text{H}$ versus $\Delta^{14}\text{C}$, where symbol colors are based on PAH concentrations. Isotopic signatures of primary sources of PAH are shown: biomass combustion (green), peat (light grey), liquid fossil fuel combustion (black), high temperature coal combustion ("high-T coal", brown) and low temperature coal combustion ("low-T coal", dark grey). Isotopic signatures on primary sources are based on reported literature values (Tables 2 and S1). Abbreviations: phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP).

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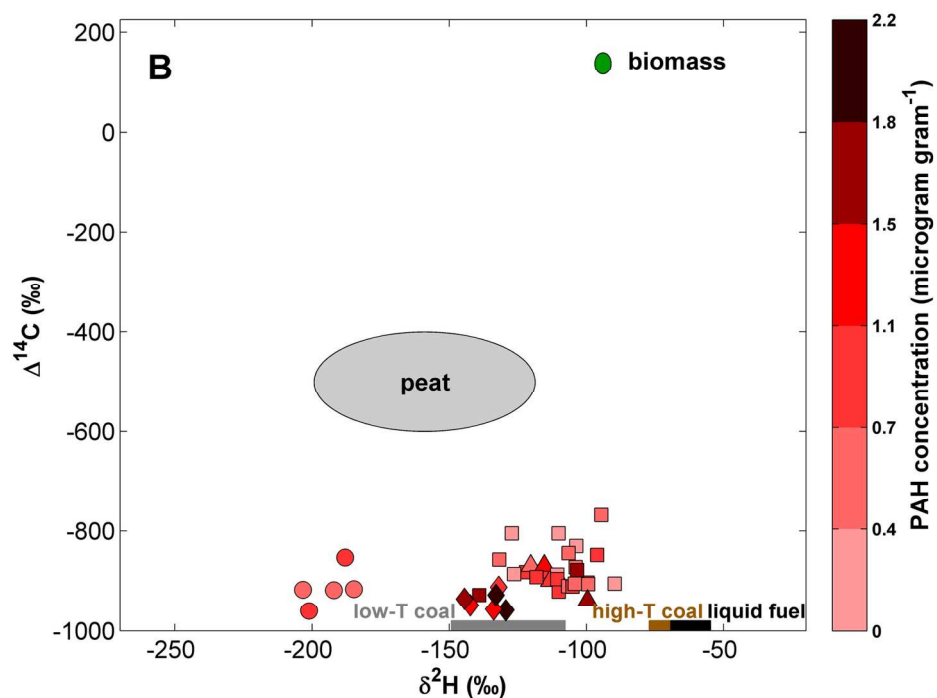


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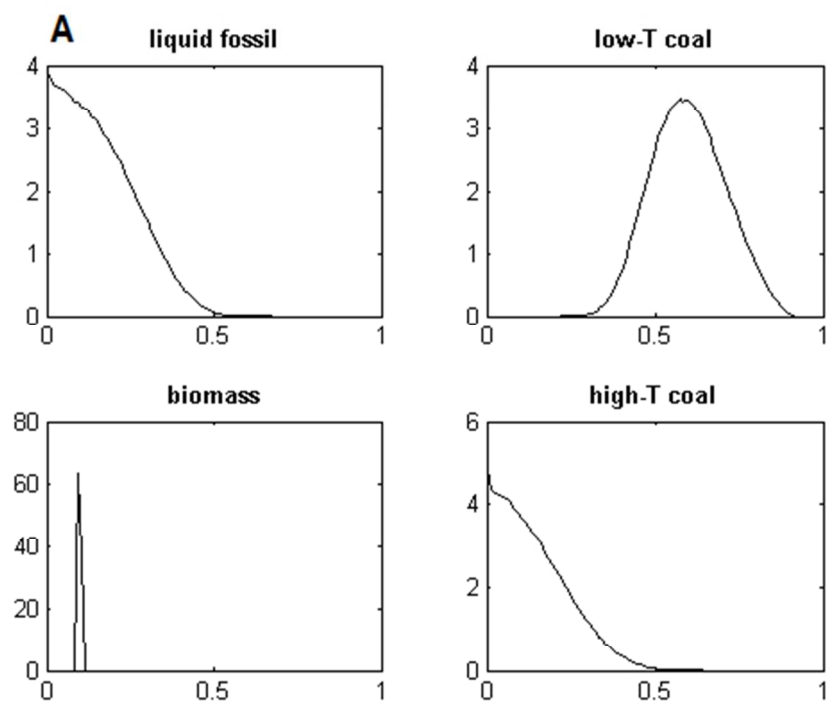


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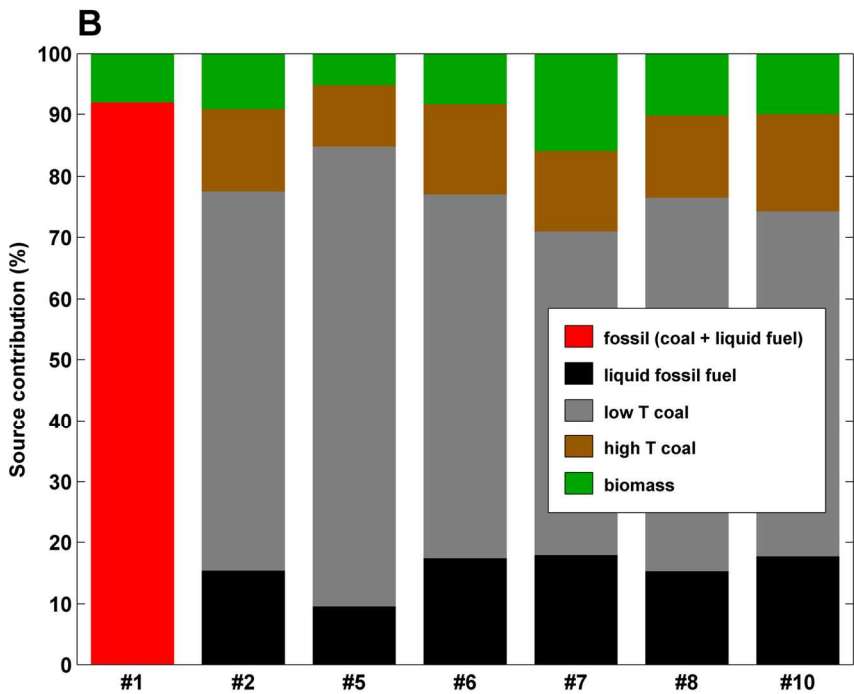


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